State of New York   )
)   Ss:
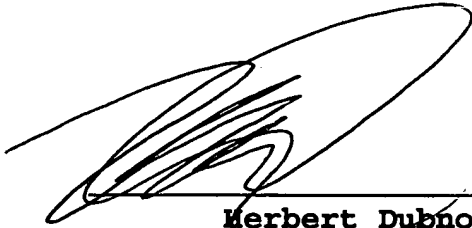County of the Bronx)

TRANSLATOR'S AFFIDAVIT

I, Herbert Dubno, a citizen of the United States of America, residing in Bronx (Riverdale), New York, depose and state that:

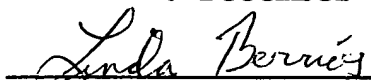I am familiar with the English and German languages;

I have read a copy of the German-language document attached hereto, namely PCT application PCT/DE03/01924 published 10 June 2003 as WO 03/106372 A1; and

The hereto-attached English-language text is an accurate translation of the above-identified German-language document.

<div style="text-align:right">

Herbert Dubno

Sworn to and subscribed before me
6 December 2004

Notary Public
</div>

LINDA BERRIOS
Notary Public State of New York
No. 01BE5016825
Qualified in Bronx County
Commission expires August 23, 2005

TRANSLATION

DESCRIPTION

HEAT INSULATING LAYER MADE OF COMPLEX PEROVSKITE

5   The invention relates to a heat insulating layer which is
made from a complex perovskite.

State of the Art

To increase the efficiency of stationary and flying gas
10   turbines increasingly higher gas temperatures are today required in
such machines. For this purpose   components of the turbine are
provided with heat insulating layers (HIL) which as a rule are
comprised of yttrium stabilized zirconium oxide ((YSZ). An
adhesion promoting layer (APL) of a MCrAlY alloy (M = Co, Ni) or
15   an aluminide layer between the substrate and the heat insulating
layer serves mainly for protecting the substrate against oxidation.
With this system, surface temperatures of the turbine elements up
to 1200°C can today be realized.

A further increase to above 1300°C is desirable but
20   however has not been realizable with the workpieces used to date,
especially with YSZ. The zirconium oxide deposited by plasma
spraying or electron beam vaporization undergoes at temperatures
above 1200°C a phase transformation as well as accelerated
sintering processes which can give rise to damage to the layer
25   within the operating time. At the same thermal conductivity of the

heat insulating layer and the same layer thicknesses, higher
surface temperatures also bring about higher temperatures in the
adhesion promoting layer and the substrate. These temperature
increases also contribute to an accelerated deterioration of the
5   bond between the materials.

For these reasons there is a world wide search for new
materials which can replace the partly stabilized zirconium oxide
as a material for a heat insulating layer.

From DE 100 56 617A1 it is known to use rare-earth
10 perovskites as heat insulating layers where La, Ce, Pr or Nd are
present in the A position and Er, Tm, Yb or Lu are present in the B
position. Such perovskites are characterized by a high melting
point which lies, depending upon the material above about 1800°C
and especially even above 2000°C. Up to the region in which the
15 material reaches its melting temperature, such a material shows no
phase transformation and thus can be used for corresponding
purposes, especially as a heat insulating layer. A further
characteristic of this aforementioned perovskite is its thermal
expansion coefficient of typically greater than 8.5×10^{-6} K^{-1}.
20 Furthermore, its reduced thermal conductivity of less than 2.2 W/mK
is advantageous for its use as a heat insulating layer.

Perovskites with these characteristics function
especially well as heat insulating layers on a metal substrate
since the thermal coefficient of expansion is matched and
25 mechanical stresses between the two materials upon a temperature

increase is limited and the reduced thermal conductivity usually limits overheating of the substrate.

Furthermore, a complex perovskite family of the general formula $A^{2+}(B^2_{1/3}{}^+B^{5+}_{2/3})O_3$ is known. These perovskites, because of

5   their temperature equalizing effect and their capacity to serve as low loss dielectrics have found use in many wireless communication devices (L. Dupont, L. Chai, P.K. Davies: "A- and B-site order in $(Na_{1/2}La_{1/2})(Mg_{1/3}Ta_{2/3})O_3$ perowskites"; A. S. Bhalla, R. Guo, R. Roy, "The perowskite structure - a review of its role in ceramic science

10 and technology", Mat. Res. Innovat. (2000) Vol. 4., 3-26).
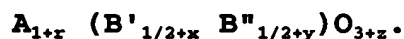

Object and Solution

The object of the invention is to provide a heat insulating material for a heat insulating layer which fulfills the requirements of a low thermal conductivity, a high thermal

15 coefficient of expansion and a high sintering temperature simultaneously with a good phase stability up to temperatures in excess of 1300°C. Furthermore it is an object of the invention to provide thermally stressed components with such a thermal insulating layer.

20 The object is achieved with a heat insulating material for a heat insulating layer with all of the features of the main claim as well as the use of this heat insulating material as a heat insulating layer on the surface of a component according to the auxiliary claim. Advantageous embodiments are given in the

25 claims dependent upon each of them.

Subject of the Invention

The subject of the invention is a thermal protective layer of a heat insulating layer with a complex perovskite pressure with a melting point above 2500°C with a thermal expansion coefficient of at least 8×10^{-6} K^{-1} and with a sintering temperature of greater than 1400°C. This heat insulating material is characterized by a complex perovskite structure in accordance with the following general formula A_{1+r} $(B'_{1/3+x} B''_{2/3+y})O_{3+z}$.

In this formula A represents at least one element from the group Ba, Sr, Ca, Be, B' represents at least one element of the group Mg, Ba, Sr, Ca, Be and B", represents at least one element of the group (TA, Nb). Alternatively the heat insulating material can also have a composition according to the following formula: A_{1+r} $(B'_{1/2+x} B''_{1/2+y})O_{3+z}$.

In this case, A can represent an element of the group Ba, Sr, Ca, Be, B' can represent at least one element of the group Al, La, Nd, Gd, Er, Lu, Dy, Tb. For B" at least one element fo the group (Ta, Nb) is selected. For both of the aforementioned compositions, such compounds should be included within the framework of this invention which have a slight deviation from the stoichiometry, than is such than $-0.1 < r, x, y, z < 0.1$.

It has been found that by contrast with many other materials of the perovskite class, these heat insulating materials have an ordered form with a layered structure in which the layers of B' and B" alternate corresponding to the stoichiometry. Also three or more atoms in the B places, again strictly maintaining the

stoichiometry, are possible, as is a mixture of the atoms in the A places. A certain deviation from the stoichiometry in the range of up to 5% is tolerable.

In addition, additives in an amount of several percent of such foreign cations which do not have ionic radii deviating excessively from those of the original cations are also possible.

The heat insulating material has advantageously a high coefficient of thermal expansion in excess of 8×10^{-6}/K and a reduced tendency to sinter. Typical sintering temperatures of these materials usually lie above 1400°C.

All heat insulating materials have a high phase stability to above 1350°C. The thermal conductivity of these perovskites is also highly satisfactory for their use as heat insulating materials since the thermal conductivity of less than 3 W/m/K is especially low and satisfactory.

In addition, the melting points of these heat insulating materials according to the invention usually lie above 2000°c and in part also above 2500°C. In addition, with these classes of materials there arises an average to large difference between the cation masses which additionally contributes to a reduction in the thermal conductivity.

All of these characteristics make the aforedescribed materials highly suitable for use as heat insulating materials.

An especially advantageous representative of the group of the aforementioned heat insulating materials is $Ba(Mg_{1/3}Ta_{2/3})O_3$.

Other compounds which have been found to be especially suitable are $Sr(Al_{1/2})Ta_{1/2})O_3$, Ca $(Al_{1/2})Nb_{1/2})O_3$, $Sr(Sr_{1/3}Ta_{2/3})O_3$ or $Sr(La_{1/2}Ta_{1/2})O3$.

A heat insulating layer made from these materials has as rule a melting point of about 3000°C and an extremely low sintering tendency.

Special Description Part

In the following, the subject of the invention is described in greater detail in connection with an exemplary embodiment and without limiting the subject of the invention thereto.

1. Characteristics of the heat insulating material.

An especially suitable heat insulating layer is obtained advantageously from the heat insulating material with the composition: $Ba(Mg_{1/3}Ta_{2/3})O_3$ which is fabricated by a solid state reaction of $BaCO_3$, MgO and Ta_2O_3. After pressing the material is sintered at 1600°C for several hours without noticeable shrinkage occurring. This material is thus suitable fur use as a heat insulating layer where a low tendency of the material to sinter is desirable.

Advantageously, it is possible to make $Sr(Al_{1/2}Ta_{1/2})O_3$ or Ca $(Al_{1/2}Ta_{1/2})O_3$ from Al_2O_3 and Ta_2O_3 and $SrCO_3$ or $CaCO_3$. In general the elements barium, strontium, and calcium, preferably as carbonates and the remaining elements preferably as oxides can be provided in a mixture. The amounts of the individual compounds are selected so that they correspond to the aforementioned

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stoichiometric composition. Using a solid state reaction, the
desired perovskite is obtained. Compositions with a slight
deviation from the stoichiometry as previously mentioned can be
made also by a suitable choice of the starting amounts.

5   With the thus produced $Ba(Mg_{1/3}Ta_{2/3})O_3$ a dilatometer test
is carried out. The figure shows the results for this material.
The heat insulating material has a coefficient of thermal expansion
at 1000°C of 10.4 x 10^{-6}/K.   This value is comparable with those
for the standard material YSZ and is highly advantageous for a use
10   of the material as a heat insulating material.

          2.   Production of a heat insulating layer system (HIS).
The heat insulating material produced by the solid state reaction
under 1. with the composition $Ba(Mg_{1/3}Ta_{2/3})O_3$ can be granulated by
spray drying and then processed by a subsequent thermal spray
15   process like atmospheric plasma spraying (APS)to an HIS system. In
this case, nickel-based or cobalt based alloy are provided by
vacuum plasma initially with an MCrAlY layer (M = Co, Ni) adhesion
promoting layer (thickness of the layer about 50 to 500 μm). Then
by atmospheric plasma spraying (APS) the heat insulating layer is
20   applied from the material according to the invention in a layer
thickness of about 50 to 3000μm. Alternatively, one can also make a
two layer thermal insulating layer in that a first layer is applied
from the YSZ material and the upper layer is then applied from the
heat insulating material (for example $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT)) by
25   deposition.

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List of the Abbreviations Used.

HIS - Heat insulating layer

YSZ - Yttrium partially stabilized zirconium oxide

APS - Atmospheric plasma spray.

5   PVD =(physical vapor deposition) = physical vapor
deposition

BMT = (Ba(Mg, Ta) O_3